PMR-15/ LAYERED SILICATE NANOCOMPOSITES FOR IMPROVED THERMAL STABILITY AND MECHANICAL PROPERTIES

Sandi Campbell[1] Daniel Scheiman[2], Michael Faile[3] and Demetrios Papadopoulos[4]

[1]NASA Glenn Research Center, Cleveland, Ohio, 44135
[2]NASA contract via QSS, [3]Earlham College, Richmond, Indiana,
[4]University of Akron, Akron, Ohio

ABSTRACT

Montmorillonite clay was organically modified by co-exchange of an aromatic diamine and a primary alkyl amine. The clay was dispersed into a PMR-15 matrix and the glass transition temperature and thermal oxidative stability of the resulting nanocomposites were evaluated. PMR-15/ silicate nanocomposites were also investigated as a matrix material for carbon fabric reinforced composites. Dispersion of the organically modified silicate into the PMR-15 matrix enhanced the thermal oxidative stability, the flexural strength, flexural modulus, and interlaminar shear strength of the polymer matrix composite.

KEY WORDS: Nanocomposite, Polyimide, Polymer Matrix Composites

1. INTRODUCTION

The durability and reliability of materials used in aerospace components is a critical concern. Among the materials requirements for these applications are a high glass transition temperature (T_g), high temperature stability in a variety of environments, and good mechanical properties over a wide range of temperatures.[1] PMR (Polymerization of Monomer Reactants)- type polyimides are thermosetting polymers which combine excellent processability, mechanical properties, and thermal oxidative stability (TOS). PMR-15 is commercially available and prepared in two stages from three monomer reactants: 2-carbomethoxy-3-carboxy-5-norbornene (nadic ester, NE), 4,4'-methylenedianiline (MDA), and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE). Curing under heat and pressure results in a highly crosslinked network structure.[2] There has been a significant amount of research aimed at increasing the TOS of PMR-15 by altering the structure of the dianhydride,[3] the diamine,[2,4-5] or the end-cap[6]. An alternative to modification of the polymer, as a means of increasing TOS, is the dispersion of a layered silicate in the polymer matrix.

This paper is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

Layered silicates have quickly become recognized as a useful filler in polymer matrix composites. Their platelet morphology and high aspect ratio results in greatly improved thermal,[7,8] mechanical,[9-11] and barrier properties.[12,13] A number of papers have reported improvements in the physical properties of thermoplastic polyimide nanocomposites.[14-16] However, the majority of work in thermosetting polymers has focused on epoxy systems.[17-19] The purpose of the research described in this paper was to investigate the TOS of PMR-15/ silicate nanocomposites, as well as evaluate the performance of PMR-15/ silicate nanocomposites as a matrix material for carbon fiber composites.

2. EXPERIMENTAL

2.1 Materials Montmorillonite (PGV-grade, CEC = 145 meq/100g) was received from Nanocor and will be referred to as PGV. Ion exchange amines: MDA, octylamine (C8), and dodecylamine (C12) were purchased from Aldrich. NE and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) were purchased from Christev. All materials were used as received.

2.2 PMR-15 Synthesis BTDE was prepared by refluxing BTDA in an amount of methanol calculated to yield a solution containing 50 wt% solids. The reflux was carried out for two hours after the solid BTDA had dissolved. Dissolution indicates the formation of the acid ester (BTDE) species. The solution was used immediately for resin synthesis.

PMR-15 resins were fabricated in several steps, as illustrated in Figure 1. The three monomers (BTDE, MDA, and NE) were dissolved in methanol (50 wt%) followed by solvent evaporation, on a hot plate, at 60° to 70°C. B-staging the mixture at 204° to 232°C in an air circulating oven produces a low molecular weight imide oligomer. The oligomer is then cured in a mold at 315°C under 2355 psi to produce the crosslinked polymer. The polymer was post cured in an air circulating oven for 16 hours at 315°C to further crosslinking. The average number of imide rings was kept constant by using a stoichiometry of 2NE/ (n+1)MDA/ nBTDE (n=2.087) corresponding to an average molecular weight of 1500.[20]

2.3 Nanocomposite Synthesis Ion exchange of the interlayer cations of PGV clay with the protonated forms of the MDA, C12, or C8 was performed by dissolving the amine (5mmol) in 450 mL of a 0.005M aqueous HCl solution at 60°C. For co-exchange of MDA with either C8 or C12, 2.5 mmol of each amine was added to the 0.005M aqueous HCl solution. The silicate (5g) was dispersed in the solution and the resultant mixture was stirred at 60°C for three hours. The solution was filtered and the clay was washed thoroughly with warm (60°C) distilled water. To maximize the amount of diamine exchanged, the procedure was repeated for a total of three exchange reactions.[21] The silicate was then dried overnight in a vacuum oven at 100°C. Throughout this paper, the clays modified with various amines will be identified by the silicate and the ion exchange amine, for example, PGV/MDA.

The procedure used to prepare PMR-15 nanocomposites was identical to that of the neat resin preparation, except that 1-7 wt% of organically modified silicate was added to the methanol solution of the monomers.
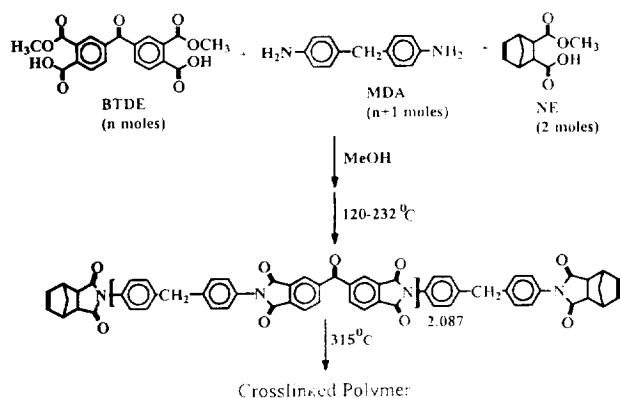
Figure 1. PMR-15 synthesis.

2.3 Characterization X-ray diffraction (XRD) patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered CuKα radiation. Ion exchanged clays, B-staged PMR-15 nanocomposites, and post cured PMR-15 nanocomposites were ground into powder and the XRD data was recorded in the range of $2\theta = 2°$ to $32°$. An increase in the basal layer spacing, which was determined from a shift in the (001) peak position, indicates ion exchange or polymer intercalation between the silicate layers. Disappearance of the (001) peak suggests an exfoliated morphology.

Transmission electron microscopy (TEM) specimens were prepared by microtoming sections of post cured PMR-15 nanocomposites, 20 to 70 nm thick, and floating the sections onto Cu grids. Micrographs were obtained with a Philips CM 200, using an acceleration voltage of 200 kV.

The glass transition temperature of post-cured PMR-15 nanocomposites was measured in air on a TA Instruments Dynamic Mechanical Analyzer (DMA). The average sample size was 17.4mm x 5.0 mm x 1.7 mm. The analysis was performed with a ramp rate of 2.5°C/min and 10 μm amplitude.

Isothermal aging of the PMR-15 nanocomposites was performed to determine the TOS. Post-cured samples were cut into 1.02 cm by 0.64 cm coupons and placed in an air circulating oven at 288°C for 1000 hours. The weight loss was measured at regular intervals by removing the coupons from the oven, allowing them to cool to room temperature, and weighing the sample.

Flexural strength, flexural modulus, and interlaminar shear strength of carbon fabric reinforced composites were measured using an Instron model 4505 and Series IX acquisition software. A 3- point flexure test, ASTM D790, was used to evaluate flexural strength and modulus. Short beam shear tests followed ASTM D2344, for measurements of interlaminar shear strength.

3. RESULTS AND DISCUSSION

Ion exchange of the interlayer cations of PGV with MDA essentially tethers one end of the diamine to the silicate, leaving the second amine free for reaction with BTDE or NE during PMR-15 synthesis. Wei et al.[16] demonstrated this as a viable method of achieving irreversible

swelling of the silicate in a thermoplastic polyimide matrix. However, previous work has demonstrated that upon ion exchange with MDA, the diamine may lie flat or folded within the silicate galleries.[22] Measurements of the PMR-15 oligomer melt viscosity suggest that incorporation of the PGV/MDA clay into the oligomer matrix tends to increase the melt viscosity and may affect the polymer structure on curing. As a result, dispersion of this organically modified silicate into a PMR-15 matrix, did not enhance the polymer thermal stability.

Ion exchange with an alkylammonium cation, such as C12, is an effective way to minimize the oligomer melt viscosity. However, the degradation temperature of C12 within the clay is approximately 200°C, well below the PMR-15 processing temperature of 315°C.[23] PMR-15 nanocomposites prepared with this material did exhibit an improvement in TOS, but the flexibility of the tethered amine, or the presence of degradation products, tended to decrease the polymer T_g.

Modification of PGV with a 1:1 molar ratio of MDA and C12 has proven to be an effective compromise. The presence of the tethered MDA allows reaction of the free amine and the polymer precursors, while the lower concentration of C12 minimizes the oligomer melt viscosity without negatively affecting T_g, shown in Table 1.

	PGV-MDA	PGV(MDA-C12)	PGV-C12
0% silicate	335	335	335
1% silicate	342	336	337
3% silicate	337	340	326
5% silicate	338	337	321
7% silicate	339	338	311

Table 1. T_g of PMR-15 and PMR-15/ PGV nanocomposites, where PGV is organically modified with MDA, MDA-C12 (1:1) or C12.

3.1 X-ray Diffraction of Organically Modified Silicate

Figure 2 shows the XRD of PGV and organically modified PGV, where the modification is MDA, C12, or MDA/C12. There is a slight increase in silicate d-spacing on ion exchange with MDA. The d_{001} peak of untreated PGV appears at $2\theta = 7.31°$ ($d_{001} = 1.21$ nm). Ion exchange with MDA shifts the peak to $2\theta = 6.37°$ ($d_{001} = 1.39$ nm). Ion exchange with C12 increases the d-spacing to $d_{001} = 1.77$ nm ($2\theta = 4.99°$). Co-exchange with MDA and C12 yields one diffraction peak at $2\theta = 6.03°$ ($d_{001} = 1.47$ nm), which is between the PGV/MDA and PGV/C12 gallery height. The presence of only one peak suggests that there is a random distribution of MDA and C12, rather than phase separated regions of each amine.
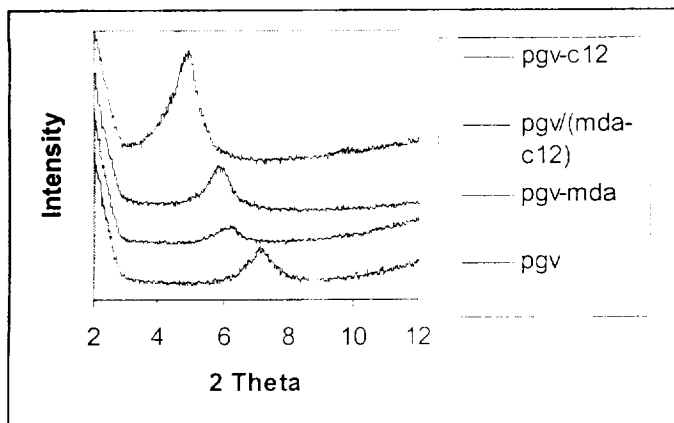
Figure 2. XRD of PGV and organically modified PGV.

For comparison, PGV was also modified with C8 and a 1:1 molar ratio of MDA and C8. While C12 is longer than the MDA chain, C8 is of a comparable length. The d_{001} peak of PGV/C8 appears at $2\theta = 6.73°$ ($d_{001} = 1.31$ nm), which is smaller than PGV/MDA. On co-exchange, the PGV/(MDA-C8) d-spacing is $d_{001} = 1.40$ nm ($2\theta = 6.28°$), similar to that of PGV/MDA.

There has been a substantial amount of research to identify the arrangement of the alkyl ammonium chain within a silicate gallery.[24-26] In general, the chains arrange into a lateral monolayer or bilayer, where they lie parallel to the silicate surface or they may extend from the surface in a paraffin-type monolayer or bilayer. The arrangement of the chains is generally dependent on the packing density, temperature, and chain length. As chain length increases, the area of a flat lying alkyl chain may become larger than the available silicate surface area. In this case a monolayer may rearrange into a bilayer.

The gallery spacing of the alkylammonium modified clays, PGV/C8 and PGV/C12, suggest that the C8 ions are arranged in a monolayer and the C12 chains are arranged in a bilayer with their alkyl chains parallel to the silicate sheets. On co-exchange of MDA and C12, the presence of the longer alkyl chain increases the gallery height beyond that observed in PGV/MDA, as a bilayer arrangement may be necessary to accommodate the long C12 chains. On co-exchange of MDA and C8, there is not an increase in gallery spacing, since the shorter chains do not occupy as much of the silicate surface area.

Nanocomposites were prepared by dispersing 2 wt% of the organically modified silicates, PGV/(MDA-C12) or PGV/(MDA-C8), into the PMR-15 matrix. The nanocomposite morphology was characterized by XRD after B-staging and after post-cure. TEM images were also obtained after post-cure. After B-staging there is a shift in the d_{001} diffraction peak of the organically modified silicate, suggesting the PMR-15 oligomers are intercalated between the silicate sheets. After post-cure, Figure 3, the diffraction peak is broadened and shifted to a lower diffraction angle. This is an indication that the ordered stacking of the silicate sheets is disrupted, but PMR-15 is generally intercalated between the silicate layers. TEM images of the post-cured nanocomposite suggest that while there are regions of disordered silicate layers, areas of stacked clay are also present, as shown in Figure 4.
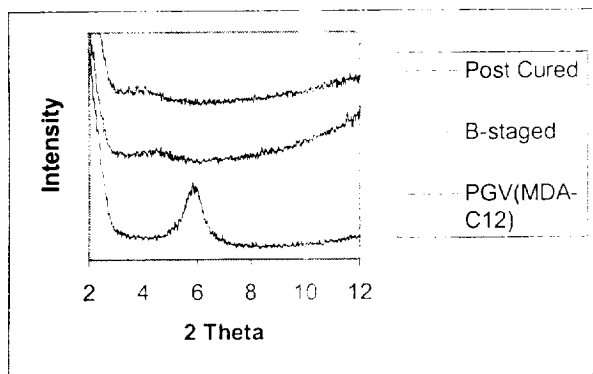
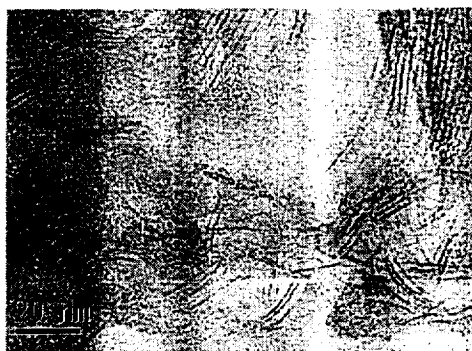Figure 3. XRD of PGV (MDA-C12) and PMR-15/ PGV/(MDA-C12) nanocomposites after B-staging and post cure.

Figure 4. TEM of PMR-15 nanocomposites containing 3 wt% PGV(MDA).

3.2 Thermal Oxidative Stability Isothermal aging studies (1000 hours in air at 288°C) of the two systems show that the TOS of the PGV/(MDA-C12) nanocomposite was an average of 8% better than PGV/(MDA-C8). Therefore, the PGV/(MDA-C12) was used for further analysis.

The concentration of PGV/(MDA-C12) dispersed in the PMR-15 matrix was increased from 0 wt% to 7 wt%. Isothermal aging data, Figure 5, shows an improvement in the TOS of the nanocomposites, with up to a 15% decrease in weight loss compared to the neat resin. The main route to degradation of PMR-15 is through oxidation of the surface layer followed by microcracking in the matrix. Microcracking allows permeation of oxygen into the bulk of the sample, furthering oxidative degradation.[27] Dispersion of the silicate in the polymer may decrease the permeation of oxygen through the bulk, thereby enhancing TOS.
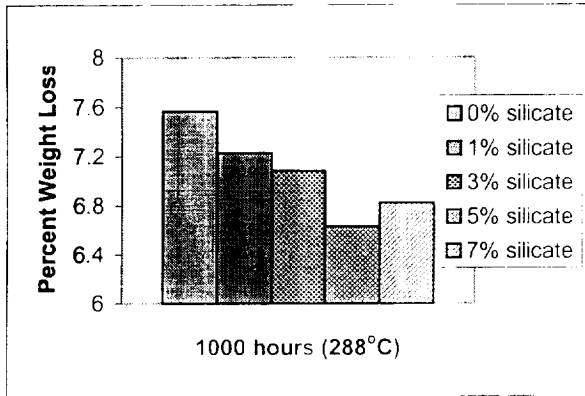
Figure 5. Percent weight loss of PMR-15 and PMR-15/ PGV(MDA-C12) nanocomposites on aging at 288°C for 1000 hours.

3.3 PMR-15/ Silicate Nanocomposite Matrix Carbon Fiber Composite

Carbon fabric reinforced composites were prepared with a PMR-15/ silicate nanocomposite matrix. The TOS of the nanocomposite matrix in comparison to that of the neat resin matrix composites were evaluated. Prepreg was prepared by brush application of the PMR-15 monomer solution onto T650-35 carbon fabric, to give a final fiber content of 60 wt%. The silicate used in the nanocomposite matrix composites was PGV/(MDA-C12). The prepreg sheets were cut into eight, 10.2 cm by 10.2 cm, plies and placed in a metal mold. The mold was heated to 232°C to imidize the monomers. The mold temperature was then raised to 315 °C, and the matrix was cured with application of 500 psi for 2 hours. The composites were post cured in an air circulating oven at 315°C for 16 hours. The TOS was evaluated by aging the specimens (2.54 cm by 1.27 cm) in an air circulating oven heated to 288°C and monitoring weight loss for 1000 hours. The data in Figure 6 shows a 5-25% decrease in the weight loss of the nanocomposite matrix composites compared to the neat resin matrix composite, after aging for 1000 hours. Unlike the neat resin nanocomposites, this data shows a decrease in the TOS of the carbon fiber composites on increasing clay concentration. This may be due to a lower extent of silicate dispersion in the carbon fiber composites. Further samples are being analyzed to verify the reproducibility of these results.
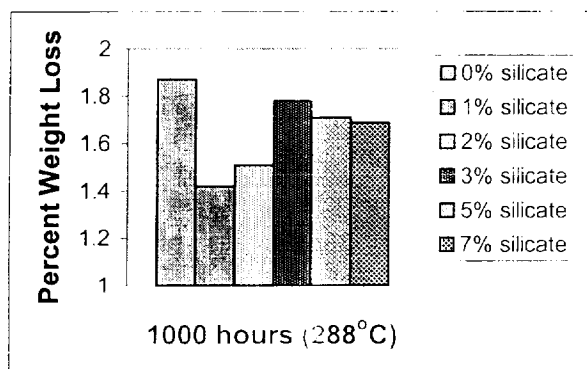

Figure 6. Percent weight loss of PMR-15 and PMR-15/ PGV(MDA-C12) nanocomposite matrix composites on aging at 288°C for 1000 hours

Mechanical tests indicated that the flexural strength, flexural modulus, and interlaminar shear strength of the carbon fiber composites increase, in some cases, using a nanocomposite matrix. Table 2 lists the room temperature and elevated temperature test results for unaged composites. As in the TOS results, the enhancement in mechanical properties is greater at the lower silicate concentrations. Table 3 lists the results of the mechanical testing of samples that have been aged for 500 hours at 288°C. In this case, the flexural modulus and interlaminar shear strength of the nanocomposite matrix composites is within experimental error of the neat resin matrix composite. However, an increase in the flexural strength of the nanocomposite matrix composites is still seen.

Sample	Room Temperature			288°C		
	Flexural Strength (ksi)	Flexural Modulus (Msi)	Shear Strength (psi)	Flexural Strength (ksi)	Flexural Modulus (Msi)	Shear Strength (psi)
0% silicate	118 ± 4	7.7 ± 0.2	9520 ± 458	79 ± 2	7.3 ± 0.3	5450 ± 129
1% silicate	138 ± 5	9.2 ± 0.1	10272 ± 152	92 ± 2	9.1 ± 0.1	6134 ± 220
3% silicate	129 ± 3	7.8 ± 0.1	9433 ± 415	86 ± 3	7.8 ± 0.2	6036 ± 217
5% silicate	123 ± 10	7.2 ± 0.1	9167 ± 205	79 ± 4	7.0 ± 0.1	6118 ± 338
7% silicate	128 ± 7	7.3 ± 0.1	8563 ± 424	79 ± 7	7.2 ± 0.1	6123 ± 479

Table 2. Mechanical properties of carbon fabric composites before aging.

Sample	Room Temperature			288°C		
	Flexural Strength (ksi)	Flexural Modulus (Msi)	Shear Strength (psi)	Flexural Strength (ksi)	Flexural Modulus (Msi)	Shear Strength (psi)
0% silicate	96 ± 6	7.2 ± 0.6	9495 ± 539	89 ± 6	7.9 ± 0.2	6235 ± 332
1% silicate	132 ± 6	9.7 ± 0.3	9127 ± 454	107 ± 3	9.8 ± 0.3	6406 ± 509
3% silicate	118 ± 9	7.9 ± 0.2	9109 ± 571	99 ± 5	8.2 ± 0.1	6290 ± 320
5% silicate	114 ± 11	7.6 ± 0.1	8551 ± 789	96 ± 4	7.3 ± 0.1	6195 ± 885
7% silicate	107 ± 2	7.7 ± 0.2	8850 ± 256	100 ± 0.2	8.0 ± 0.1	6570 ± 227

Table 3. Mechanical properties of carbon fabric composites after aging at 288°C for 500 hours.

4. CONCLUSIONS

Silicate modification by co-exchange of an aromatic diamine and a long chain alkyl amine is an effective method to enhance PMR-15 TOS without compromising the T_g. Dispersion of PGV/(MDA-C12) in the matrix of a PMR-15/ carbon fiber composite results in a significant increase in the TOS and mechanical properties of the composite. Thus, use of nanocomposites as matrix resins is a viable approach to the development of polymer matrix composites with improved high temperature stability.

5. ACKKNOWLEDGMENTS

6. REFERENCES

1. M.A. Meador, Annu. Rev. Mater. Sci., **28**, 599 (1998).
2. P. Delvigs, D.L. Klopotek and P.J. Cavano, High Perform. Polym., **6**, 209 (1994).
3. W. Alston, High Perform. Polym., **7**, (1), 93 (1995).
4. P. Delvigs, D.L. Klopotek and P.J. Cavano, High Perform. Polym. **9**, 161 (1997).
5. K. Chuang, J. Waters and D. Hardy-Green, 42nd Intnatl. SAMPE Symp, **42**, 1283 (1997).
6. M.A.B. Meador, et. al., Chem. Mater., ASAP Article, (2001).
7. H.-L. Tyan, Y.-C. Liu and K.-H. Wei, Chem. Mater., **11**, 1942 (1999).
8. H.-L. Tyan, Y.-C. Liu and K.-H. Wei. Polymer, **40**, 4877 (1999).
9. T. Lan and T.J. Pinnavaia, Chem. Mater., **6**, 573 (1994).
10. M. Kawasumi, et. al., Macromolecules, **30**, 6333 (1997).
11. T.-K. Chen, Y.-I., Tien and K-H. Wei, Polymer, **41**, 1345 (2000).
12. S. Burnside and E.P. Giannelis, Chem. Mater., **9**, (7), 1597 (1995).
13. P. Messersmith and E.P. Giannelis, J. Polym. Sci. A: Polym. Chem., **33**, 1047 (1995).
14. K. Yano, et. al., J. of Poly. Sci., Part A., Poly. Chem., **31**, 2493 (1993).
15. H.L. Tyan, K.H. Wei and T.E. Hsieh, J. of Poly. Sci., Part B., Poly. Phys., **32**, 2873 (2000).
16. H.L. Tyan, Y.C. Liu and K.H. Wei, Chem. Mater., **11**, (7), 1942 (1999).
17. T. Lan and T.J. Pinnavaia, Chem. Mater., **6**, 2216 (1994).
18. Z. Wang, T. Lan, and T.J. Pinnavaia, Chem. Mater., **8**, 2200 (1996).
19. T. Lan, D. Kaviratna and T.J. Pinnavaia, Chem. Mater., **7**, 2144 (1995).
20. T. Serafini, P. Delvigs and G. Lightsey. J. Appl. Poly. Sci., **16**, 905 (1972).
21. H. Shi, T. Lan and T.J. Pinnavaia, Chem. Mater., **8**, 1584 (1996),.
22. S. Campbell and D.A. Scheiman, High Performance Polymers, submitted.
23. W. Xie, et. al., Chem. Mater., **13**, 2979 (2001).
24. A. Usuki, et. al., J. Mater. Res., **8**, (5). 1174 (1993).
25. M. Ogawa and K. Kuroda, Bull. Chem. Soc. Jpn., **70**. 2593 (1997).
26. R. Vaia, R. Teukolsky and E.P. Giannelis, Chem. Mater., **6**, 1017 (1994).
27. M.A.B. Meador, et. al., High Perfor. Polym., **8**, 363 (1996).